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Submission date: 11-Aug-2018 04:38AM (UTC+0700)
Submission ID: 989045710
File name: AIP_conference.pdf (1.18M)
Word count: 4004
Character count: 20269

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Citation: AIP Conference Proceedings **1699**, 060001 (2015); doi: 10.1063/1.4938355
View online: http://dx.doi.org/10.1063/1.4938355
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1699?ver=pdfcov
Published by the AIP Publishing

Selective Transport of Fe(III) using Ionic Imprinted Polymer (IIP) Membrane Particle

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Abstract. The membrane particles was prepared from polyvinyl alcohol (PVA) and polymer IIP with weight ratios of 1: 2 and 1: 1 using different adsorbent templates and casting thickness. The permeability of membrane towards Fe(III) and also mecanism of transport were studied. The selectivity of the membrane for Fe(III) was studied by performing adsorption experiments also with Cr(III) separately. In this study, the preparation of Ionic Imprinted Polymer (IIP) membrane particles for selective transport of Fe (III) had been done using polyeugenol as functional polymer. Polyeugenol was then imprinted with Fe (III) and then crosslinked with PEGDE under alkaline condition to produce polyeugenol-Fe-PEGDE polymer aggregates. The agrregates was then crushed and sieved using mesh size of 80 and the powder was then used to prepare the membrane particles by mixing it with PVA (Mr 125,000) solution in 1-Methyl-2-pyrrolidone (NMP) solvent. The membrane was obtained after casting at a speed of 25 m/s and soaking in NaOH solution overnight. The membrane sheet was then cut and Fe(III) was removed by acid to produce IIP membrane particles. Analysis of the membrane and its constituent was done by XRD, SEM and size selectivity test. Experimental results showed the transport of Fe(III) was faster with the decrease of membrane thickness, while the higher concentration of template ion correlates with higher Fe(III) being transported. However, the transport of Fe(III) was slower for higher concentration of PVA in the membrane. IImparticles works through retarded permeation mechanism, where Fe(III) was bind to the active side of IIP. The active side of IIP membrane was dominated by the –OH groups. The selectivity of all IIP membranes was confirmed as they were all unable to transport Cr (III), while NIP (Non-imprinted Polymer) membrane was able transport Cr (III).

Keywords:IIP Membrane particle, polyeugenol, functional polymer, selective transport of Fe.

INTRODUCTION

In the last decade, imprinting techniques is used for the buildup of molecularly imprinted membranes (MIMs) that can selectively recognize target molecule in a solution during a simple static adsorption as well as permeation through a membrane device [1].

The transport of metal ions had been studied as a form of separation, saturation and recovery for both precious and toxic metals. This study was driven by the environmental concerns and the decrease of natural resources. With site-specific receptors incorporated into imprinted membrane, the membrane will then have specific transport or penetration routes, pores or matrices through only the desired ions will be able to pass [2].

MIMs are membranes that can either IIPs contain IIPS. There are three main strategies that can be used to synthesize MIM [3-4]: (1) sequential approach preparation of membrane from IIP_S that had been prepared using conventional method; (2) simultaneous formation of IIP structure and membrane morphology; and (3) Sequential

International Conference of Chemical and Material Engineering(ICCME) 2015
AIP Conf. Proc. 1699, 060001-1–060001-10; doi: 10.1063/1.4938355

approach preparation of IIP using supporting membrane with morphology. Djunaidi et al (2015) have synthesized IIP membrane via simultaneous formation of IIP stucture and morphology (insitu) [5].

In the present study, the synthesis of MIM from IIP particles had been studied. Membrane preparation was preceded by the synthesis of IIP (IIP) Fe(III) using polyeugenol as the functional polymer and PEGDE as the crosslinker. The IIP was then used to synthesize the membrane using PVA as the membrane base. PVA membranes usually display high stability in strongly acidic and alkaline environments [6-7]. PVA is usually used for dehydration when swelling due to water adsorption becomes a problem [8]. However, PVA is a poor conductor for protons as it does not have any negative charge such as carboxylic group or sulfonic acid groups [9].

EXPERIMENT

Materials And Instruments

Instruments

The instruments used in this study are pH-meter, magnetic stirrer, separatory funnel, glasswares and plastic wares, analytical balance (Mettler Toledo AB54-S), three-necked flask, casting machine (Erichsen), FTIR Spectrophotometer (Jasco Miracle ATR), XRD (Shimadzu XRD-8000), AAS (Atomic Absorption Spectrophotometry (Shimadzu 8201PC), UV visible 50 Probe, TOC- analyser (SHIMADZU), a set of difussion transport cell..

Materials

The materials used in this study are Eugenol, $BF_3O(C_2H_5)_2$and PEGDE (Polyethyleneglycoldiglycidyl ether) that were purchased from SIGMA-Aldrich, 1 Methyl 2 pyrrolidone and Fe(III) nitrat nonahydrate were purchased from Fluka, NaOH, HCl, polivinilalkohol (PVA, Aldricht Mr. 125000), aquademineralized (Milli-Q).

Methods

Synthesis of Polymers

Polyeugenol. Eugenol (5.8 g) was put in a 3-necked flask, then 0.25 mL of boron trifluoride diethyl ether, $BF_3O(C_2H_5)_2$ was added as catalyst. The addition was done 4 times every hour while stirring with magnetic stirrer at room temperature. The occurrence of a reaction can be characterized by the color change of the solution into red. After the last addition of the catalyst, the polymerization was allowed to continue up to 12-16 hours, after which 1 mL of methanol was added to stop the reaction. The gel produced was dissolved in chloroform and put into a separating funnel and then washed repeatedly with distilled water until neutral. The organic layer was transferred into a 50 mL erlenmeyer flask and added with anhydrous Na_2SO_4. The liquid was separated by decantation. Afterwards, the solvent was evaporated in rotary evaporator at 40 °C. The residue obtained was further dried in the desiccator, and was subsequently weighed and characterized using FT-IR.

Synthesis of IIP-Fe(III) Membrane Particles

Polyeugenol (0.5 g) was stirred with (Fe (III) solution with different concentrations for 24 hours. The product was filtered with a filter paper and subsequently air dried at room temperature. 0.3 g of Polyeugenol-Fe(III) produced from this process was then crosslinked using PEGDE as the crosslinker with a mole ratio of 1:1 by heating for 15 minutes at 80-90 °Cwith 20 mL 1M NaOH as catalyst. The product was then neutralized and dried at 115°C in an oven for 6 hours. The polymer produced was further treated with acid for 24 hours to release the Fe(III) ions and form the final product of IIP-Fe(III) polymer.

The preparation of IIP membrane particles.

0.25 g of IIP Fe was added with 0.5 g PVA (weight ratio of IIP:PVA was 1:2) and dissolved in 7 mL NMP and then heated at 100-100 oC for 4 hours. Next, casting was carried out at 25m/s on a glass layer. The casting layer was then dried in an oven at 80 °C overnight. The membrane produced was then coagulated in 1M NaOH solution overnight. Before mounted onto the ring of the diffusion cell, the membrane sheet obtained was cut and then neutralized with demineralized water, after which it is soaked in 0.1 M HCl overnight to leach the metal ions. Afterwards, the membrane was washed with demineralized water and then mounted on the diffusion cell.

Synthesis of Non-Imprinting Polymer (NIP) membrane.

NIP was synthesized using similar method as the synthesis of IIP, excluding the step of Fe(III) binding to the polymer.

Transport of Fe(III) ion through the membrane.

The transport of Fe(III) ion through the membrane was carried out in a difussion cell, using 50 mL Fe(III) solution at pH 3 in the feed phase.

Performance test for the Fe(III) IIP membrane particles.

Optimization of Fe(III) IIP membrane performance was done for different membrane thickness, templates and PVA weight.

Selectivity test for IIP membrane particles.

The selectivity of IIP membrane was compared to that of NIP membrane and the test was carried out using 50 mg/L Cr(III) solution in separate systems.

Total Organic Carbon (TOC) measurement.

Diffusion measurements were performed to determine the rate of diffusion through the corresponding membranes (effective diffusion coefficient) and the solute fractionation under these conditions. This measurement was carried out using a diffusion cell composed of two half-cells. The membrane was fixed between these half-cells with the membrane side. The two half cells were filled at the same time to the same height level with receiving solution (water; 50 ml) and feed solution (10 g equimass mixture of dextrans with average molecular weight of 15000 until 20000 (dextran 15) in water ; 50 ml) and stirred at the same stirring rate. The diffusion of dextran through the membrane was monitored by measuring the concentrations using TOC in both half-cells at 24 hours.

Analysis of Fe(III).

The analysis of Fe(III) was done by UV-visible spectrophometer using KSCN reagent at 458 nm and Atomic Absorption Spectrophotometry (AAS).

Analysis of Cr(III) with UV-Visible spectrophotometer.

The analysis of Cr(III) was done by UV-Visible spectroscopy at 420 nm.

RESULTS AND DISCUSSIONS

Synthesis of IIP Fe Membrane Particle

As can be seen in Fig 1, the synthesis of IIP-Fe Membrane comprises of four stages, starting with the polymerization of eugenol. Eugenol was polymerized using BF_3 diethyl ether as catalyst, and the resulted polyeugenol was characterized by FT-IR and NMR. To determine how many *n* of eugenol molecules exist in the polyeugenol chain, gel permeation chromatography (GPC) analysis was done [10]. The polyeugenol was used for the synthesis IIP Membrane particle. This was done by uploading Fe(III) into the polyeugenol chain, followed by crosslinking using PEGDE. The polymer produced was further treated with acid for 24 hours to release the Fe(III) ions and form the final product of IIP-Fe(III) polymer. The results of the polymerization as well as its characterization had been reported elsewhere. The IIP-Fe(III) polymer was then crushed and sieved using 60 mesh particle size and then mixed with PVA in NMP solvent using weight ratio of 1:2 and 1:1.

XRD Analysis

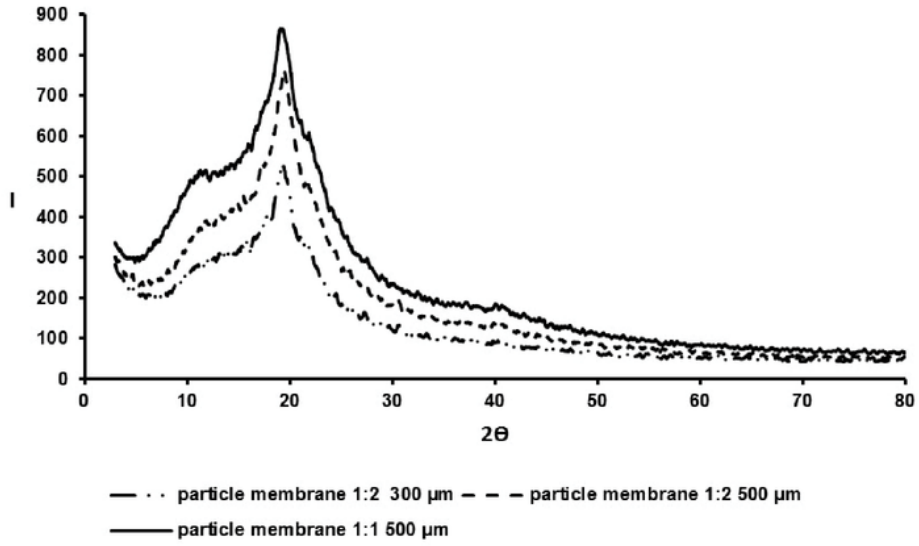


FIGURE 1. X-ray difractograms of the membrane particles

Figure 1 shows that the higher IIP content, the higher the crystallinity of the membrane. Membrane with 0.5 g IIP and 0.5 PVA (weight ratio of 1:1) has higher crystalline intensity than that with 0.25 IIP and 0.5 g PVA (weight ratio of 1:2, membrane thickness of 500 µm) and 0.25 g IIP and 0.25 g PVA (weight ratio of 1:2, membrane thickness of 300 µm)

The transport of Fe(III) in the IIP membrane particles

The study of Fe(III) transport was carried out through a series of experiment using 25 mg/L Fe(III) solution at pH 3 and 0.1 HCl solution as the stripping phase. The result of Fe (III) transport from the feed phase to the stripping phase can be seen in Fig 2.

It can be seen in Fig 2 that the concentration of Fe(III) in the feed phase decreased with time as Fe(III) was transported to the stripping phase so that the concentration of Fe(III) in the stripping phase increased with time. It can also be inferred from Figure 2 that there are still a number of Fe(III) ions that are still trapped in the membrane, which means that the membrane thickness needs to be reduced.

Variation of template concentration

Template is one of the most important parts of IIP as well IIP particles, as ilustrated in Fig 2.

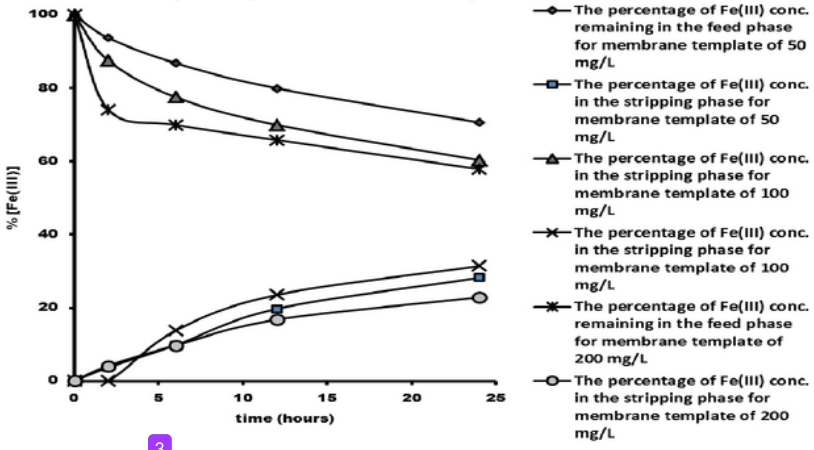


FIGURE 2. Transport percentage of Fe(III) in the feed phase and stripping phase for 500 µm membrane with different template concentration

It can be seen in Fig 2 that the transport percentage of Fe(III) from the feed phase increased with increasing template concentration for both 300 µm and 500 µm membranes. Interestingly, the concentration of Fe(III) in the stripping phase decreased with increasing template concentration, which suggests that at higher template concentration, more imprinted caves were formed in the membrane which resulted in stronger interactions between the membrane and Fe(III) ions, so that the ions are more difficult to be released.

Variation of membrane base (PVA) amount

To determine the effects of membrane base (PVA) amount, a series of Fe(III) transport experiments were carried out for IIP membrane particles synthesized with different PVA concentration. The weight ratio used for IIP polymer: PVA were 1:2 and 1:1, and the transport experiments results can be seen in Fig 3.

It can be seen from Fig 3 that the transport percentage of Fe(III) in the stripping phase slightly increased with decreasing PVA concentration.

Permeability

Based on the assumption suggested by Nghiem [11], the decrease of Fe(III) concentration in the feed phase can be described in the following equation:

$$AJ_s = -V_s \frac{dCs}{dt}\, dt \tag{1}$$

At initial condition,

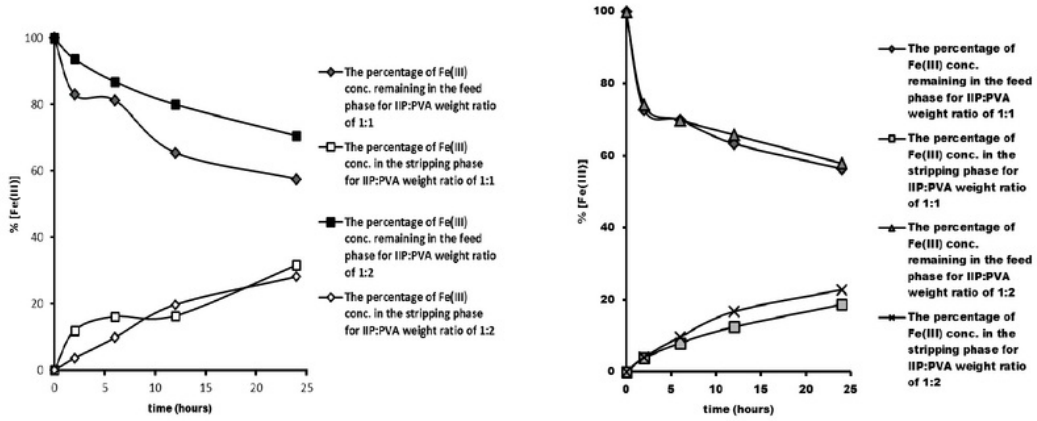
$$C_s = C_s^o \text{ at } t=0 \tag{2}$$

Meanwhile, the transport of Fe(III) through the membrane can be described by the following equation:

$$J_s = P_s C_s \tag{3}$$

So that the equation for the solution becomes:

$$\ln\left[\frac{Cs}{C_s^o}\right] = \left[\frac{A}{Vs}\right] P_S\, t \tag{4}$$



(a) (b)

FIGURE 3. The comparison of Fe(III) transport percentage in the feed phase and stripping phase for membrane template (a)100 mg/L (b) 200 mg/L and membrane thickness of 500 µm, with of IIP polymer : PVA weight ratio of 1:2 and 1:1

Permeability can be calculated using equation (d). From this study, the permeability of MIMs in the feed phase was measured after transport for 24 h, and calculation results can be seen in Table 1.

TABLE 1. Permeability of different membrane particles

Types of Membrane	Permeability$\times 10^{-8}$ (m/s)
Membrane Template 50 1:2 300 µm	130
Membrane Template 50 1:2 500 µm	64
Membrane Template 50 1:1 500 µm	102
Membrane Template 100 1:2 300 µm	118
Membrane Template 100 1:2 500 µm	92.1
Membrane Template 100 1:1 500 µm	144
Membrane Template 200 1:2 300 µm	151
Membrane Template 200 1:2 500 µm	128
Membrane Template 200 1:1 500 µm	185
NIP 300 µm	129
NIP 500 µm	104

It can be seen from Table 1 that the permeability of the membrane particles confirmed the results obtained from the different conditions used for the experiments. Meanwhile, the flux of the MIMs after 24 hours can be seen in Fig 4. It can be seen in Fig 4 that the flux is in line with the membrane permeability, which confirms that flux is proportional to permeability [11].

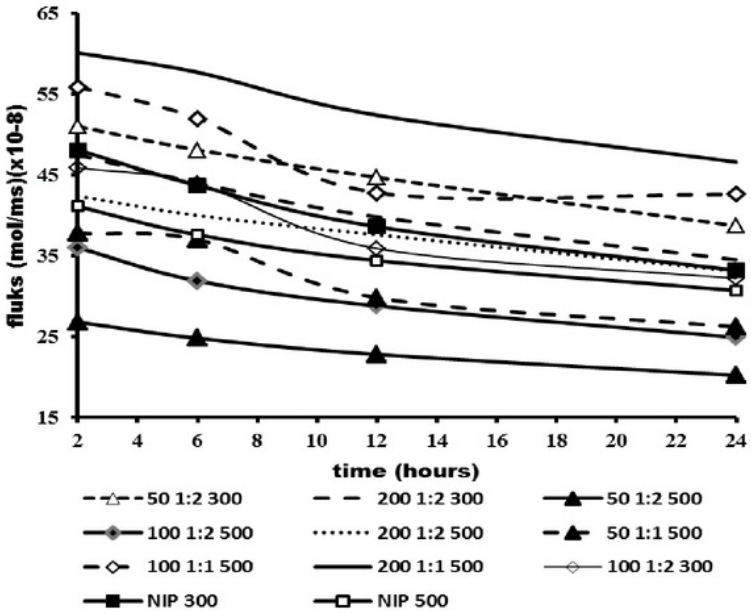


FIGURE 4. The transport percetage of Fe(III) in the feed phase and stripping phase of the membrane template 200 and 500 µm with weight ratio of 1:2 and 1:1

Scaning Electron Microscope (SEM) Analysis

The complete results form SEM analysis are shown in Fig 5.

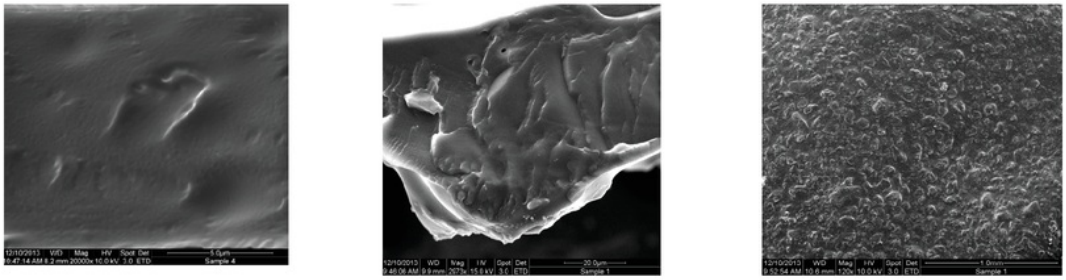


FIGURE 5. The results from SEM analysis of IIP membrane particles. (a). cross-section of the membran membran template 100 500 µm after transport Fe (250x magnification); (b). Front side of membrane template 200 500 µm after transport of Fe (120x magnification) (c).coss-section of membrane template 200 500 µm after transport of Fe (2973x magnification)

As can be seen in Fig 5, the membrane particles appeared to be solid and unporous as well as symmetical. This is probably because the pores in IIP are blocked by the membrane base (PVA). This result was confirmed by the results obtained from size selective analysis using TOC analysis

Size selective analysis using TOC

TABLE 2. Size selective analysis using TOC

	TOC	
Types of membrane (300 μm)	% dextran remaining in the feed phase	% dextran in the water phase
Membrane template 200	99.42	0.58
NIP	93.76	0.98

As shown in Table 2, the membrane with 200 mg/L template could barely transport dextran 15, while NIP was able to transport almost 6% of dextran 15. This means that the membrane particles are nearly poreless, while the pores in NIP is larger that those in the membrane template particles 200

Membrane Selectivity

The selectivity of the membrane was determined using 50 mg/L of Cr(III) solution. Cr(III) was selected because it has the same charge as Fe(III) and thus is expected to have similar charge density as well as ionic radius to Fe(III) [12]. The result obtained from the selectivity study can be seen in Table 3.

TABLE 3. Transport percentage of Cr(III) for different membrane particles

Type of membrane (IIP particles with 300μm and weight ratio of 1:2)	% tranport of Cr(III)
NIP	12.97
Membrane template 50	0
Membrane template 100	0
Membrane template 200	0

As shown in Table 3, none of the MIMs was able to transport Cr(III), while NIP was still still able to transport Cr(III) to a certain extent, indicating the selectivity of MIMs synthesized in our study

Transport Mechanism

There are two main mechanisms that can be used to analyze the selective transport of ionic metal through imprinted membrane: (i) permeation facilitated by preferential affinity for the transport of the target molecule, so that the transport of competing ions will be prohibited and slower, and (ii) delayed permeation due to very strong affinity toward the target molecules while the transport of other molecules is relatively faster until IIP sites is saturated with the target molecule [3-4]. Slow adsorption of templates occurred due to the facilitated adsorption on the binding sites of IIP membrane for other molecules/ions. Facilitated transport template occurred due to interaction between the template and the binding sites of IIP membrane so that the template can be used for selective transport [3-4].

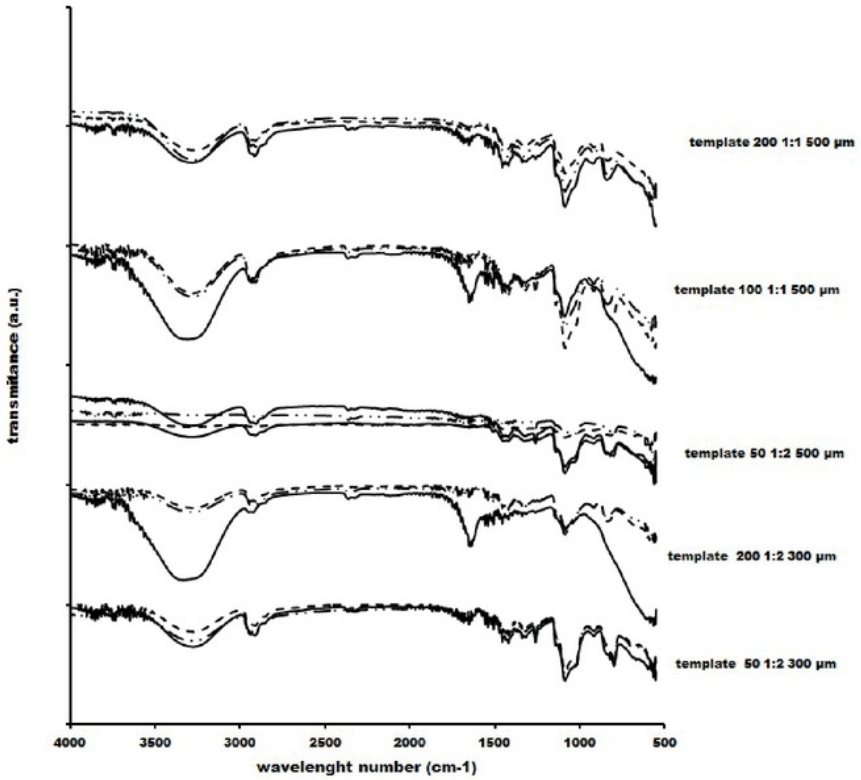


FIGURE 6. Infrared spectra of different IIP membrane particles before and after contact with metal ion solution (____) Infrared spectra of initial membrane (before contact) (- - - -) Infrared spectra of the membrane after contact with Fe(III) and Cr(III) (_ · · _ · · _)

It can be seen form Infrared spectra in Fig 6, the absorption band for –OH group at 3300 cm^{-1} before contact is both sharper and wider than after contact with either Cr(III) or Fe(III), which means that it is possible that the MIMs used the –OH groups to bind with both metal ions.

CONCLUSIONS.

MIM particles prepared from PVA as membane base, IIP particles and polyeugenol as functional polymer and NMP as solvent can be used for the transport of Fe(III). A number of factors were found to influence the performance of the MIM particles being synthesized, such as membrane thickness, template ion concentration, and the weight of the membrane base (PVA) used in the synthesis. The flux of Fe(III) was found to increase with the decrease of membrane thickness and the weight of the membrane base. In addition, MIM particles works through retarded permeation mechanism, where Fe(III) was bind to the active side of IIP. The active side of IIP is dominated by the –OH groups. The MIM particles synthesized is also selective, as demonstrated by the selectivity test using Cr(III), in which Cr(III) could not be transported, which differs from NIP which was was able to transport some of the Cr(III) ions.

ACKNOWLEDGMENT

The authors would like to express sincere gratitude to the Government of the Republic of Indonesia for the Sandwich Program.

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